APPLICATION

FOR

UNITED STATES LETTERS PATENT

TITLE: MEASUREMENTS OF ELECTROMAGNETIC
PROPERTIES AND INTERACTIONS BASED ON
RADIATION-EXCITED POLARIZATIONS
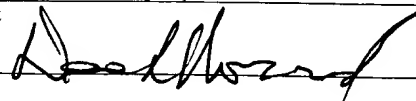
APPLICANT: DANIEL P. WEITEKAMP

MEASUREMENTS OF ELECTROMAGNETIC PROPERTIES AND INTERACTIONS BASED ON RADIATION-EXCITED POLARIZATIONS

This application claims the benefit of U.S. Provisional Application No. 60/135,244, filed on May 21, 1999.

BACKGROUND

This application relates to measurements of electromagnetic properties and interactions of various materials, and more specifically, to techniques and systems for measuring electromagnetic properties and interactions based on radiation-excited polarizations.

Various materials respond to an external radiation field, e.g., an electromagnetic irradiation, to develop electromagnetic polarization. The interaction between the induced polarization in a material and the radiation field can be measured or monitored to provide useful information for a variety of applications including, among others, imaging, spectroscopy, recording, and determination of distances and angles. Non-destructive measurements based on such interaction of high spatial resolution and detection sensitivity are particularly desirable. A number of techniques have been developed to meet such needs. Examples include the scanning tunneling microscope, atomic force microscope, and near-field scanning optical microscope.

Many of such techniques operate based on detection of electromagnetic emission from a sample under excitation of an

external field.   In incoherent spontaneous emission, the

signal to be detected is essentially determined by the

multiplication of the average excited state population and the

rate of emission. In methods based on coherent emission, it is

5   useful to describe the detection as being of those field modes

into which the sample has radiated. In both cases, the

detection sensitivity is generally limited by the quantum

limit of the "shot noise" that is inherent in the detection.

SUMMARY

The present techniques and systems include a method of

creating and detecting a force interaction between a sample

and a probe to measure properties of the sample. A probe

excitation field is generated to at the probe formed of a

15   polarizable material. This produces a probe polarization.

The sample with a sample polarization is placed in a field of

the probe polarization effectuate an interaction between the

probe and the sample. A mechanical oscillator is engaged to

at least one of the probe and the sample and moves in response

20   to said interaction. The motion of the oscillator is then

detected and is used to measure a property of the sample.

DESCRIPTION OF DRAWINGS

FIG. 1 shows one embodiment of a force-detected optical spectrometer.

FIG. 2 shows one exemplary arrangement of the sample and
5   the probe.

FIG. 3 shows one implementation of the system shown in FIG. 1.

DETAILED DESCRIPTION

10   FIG. 1 shows a system 100 having a probe module 101, a detection module 103, and a processing module 105 for measuring the electromagnetic properties and interaction of a sample 110 according to one embodiment. This system can operate as a force-detected optical spectrometer ("FDOS") to

15   measure properties of the sample 110 or as an imaging device to produce an image of the sample 110. The probe module 101 includes a sample holder 112 to hold the sample 110 for measurement. A probe 120 is provided to interact with a desired location on the sample 110 through electromagnetic

20   coupling. The force response of either the probe 120 or the sample 110 due to the interaction between the probe 120 and the sample 110 is then measured by the detection module 103. The processing module 105, which may include a microprocessor, then receives and processes the detection signal from the

25   detection module 103 to produce useful information about the

sample 110. The probe module 101 may also include a

positioning mechanism such as a position scanner to control

the relative position of the probe 120 with respect to the

sample 110 so that different locations on the sample 110 can

5   be measured. In addition, two or more probes may be

implemented in the probe module 101 to measure different

locations at the same time.

The probe 120 generally includes a material that can be

polarized by an external probe excitation radiation 121, e.g.,

10   a metal or a dielectric. Hence, the polarization induced in

the probe 120 can produce a radiation field to interact with

the sample 110 by producing a force on the sample 110 and a

counter force on the probe 120. The probe module 101 is

designed to produce two mutually coherent excitation radiation

15   waves 111 and 121 at two different frequencies. The sample

excitation wave 111 at an angular frequency ω_s is used to

excite a sample polarization in the sample 110 at the same

frequency ω_s. The angular frequency ω_p of the probe

excitation wave 121 is generally different from ω_s and is used

20   to excite a probe polarization in the probe 120 at the

frequency ω_p. One of the radiation waves 111 and 121 may be a

static field (i.e., ω_s or ω_p is zero).

Hence, when the probe 120 is sufficiently close to the

sample 110, the induced polarization in the sample 110

25   experiences a field produced by the induced polarization in

- 4 -

the probe 120. Accordingly, this field produces a force on the sample 110. This force is a function of the frequencies ω_s and ω_p through the response of the sample and probe to the corresponding waves. In a first-order approximation, the

5 force oscillates at the difference frequency $\omega_f = |\omega_p - \omega_s|$. Similarly, the induced polarization in the probe 120 experiences a field produced by the induced polarization in the sample 110 and experiences a force opposite in its direction to the force on the sample 110. The force on either

10 the sample 110 or the probe 120 can be measured to determine the electromagnetic properties of the sample 110 and to produce an image of the sample 110.

The interaction force between the sample 110 and the probe 120 can be measured by a displacement of either the

15 sample 110 or the probe 120 caused by the force. For example, when one of the sample 110 and the probe 120 is fixed and the other is engaged to a mechanical oscillator, the displacement of the oscillator will change in accordance with the interaction force. Hence, the amplitude of the oscillator can

20 be measured to determine the electromagnetic properties of the sample 110. When the modulation frequency ω_f is tuned near the resonance frequency ω_h of the oscillator by adjusting either ω_s or ω_p, the response of the oscillator becomes highly sensitive to the force and hence can be used to achieve high

25 detection sensitivity. Therefore, the excitations of the

sample 110 and the probe 120 at different frequencies provides
a conversion mechanism to convert a material polarization
signal at a high frequency ω_s into a low-frequency signal at
$\omega_f = |\omega_p - \omega_s|$ within the frequency range of the mechanical

5   oscillator. This is only one operation mode of the system
100. Other operation modes are also possible and are
described below.

The induced polarizations in the sample 110 and the probe
120 may include any polarizations. The implementations of the
10   probe module 101 and the detection module 103 may vary with
the nature of the polarizations, such as electric or magnetic
polarizations, dipolar or quadrupolar polarizations, or the
dependence of the amplitude of the interaction force on
various incident fields, e.g., a linear dependence on one or
15   more incident field amplitudes. The force measurements may
also include effects of elastic contributions which shift the
frequency of the oscillator and of dissipative contributions
which damp its motion.

The probe module 101 may operate in a near field
20   configuration where the spacing between the sample 110 and the
probe 120 is less than one wavelength of any of the radiation
waves used. Hence, the sample 110 and the probe 120 are
within each other's evanescent fields of the induced
polarizations. This configuration provides a strong
25   interaction between the sample 110 and the probe 120. In

addition, this configuration can be used to achieve a spatial resolution higher than the spatial resolution in a far-field configuration where the spacing between the probe 120 and the sample 110 is much greater than one wavelength of any of the

5   radiation waves involved. In particular, mechanical oscillators with one or more dimensions small compared to the free space wavelength of such radiation may be used in a near-field configuration.

     This use of close proximity of polarizable objects

10   increases their force of interaction. This proximity, combining with the use of small mechanical oscillators with high force sensitivity, allows sensitivity and spatial resolution that can be qualitatively better than many other spectroscopic methods. The ability to apply this force of

15   interaction at chosen mechanical frequencies leads to advantages over methods in which the DC force is measured. The use of possibly different incident fields in sample and probe volumes and/or their different response to common incident fields allows separate optimization of each

20   polarization and a great variety of modulation schemes. In addition to modulation of the incident fields in order to achieve a desired mechanical resonance, the properties of the sample, the probe and their geometry relative to one another or relative to other fields may also be modulated.

25   The calculation of the force on the oscillator follows from established principles of electromagnetism and its

interaction with matter. By using polarizable probe material in close proximity to the sample, large gradients in the near field of matter can be achieved to enhance the interaction and the detection sensitivity.

5   FIG. 2 illustrates one way of the exciting the sample 110 and the probe 120 with radiation waves when the contributions from electric-dipole transitions dominate the induced polarizations in both the sample 110 and the probe 120. The interaction energy H between the sample 110 and the probe 120

10 can be written as:

$$H = -\int \vec{E}_s \cdot \vec{P}_p dV_p \quad = -\int \vec{E}_p \cdot \vec{P}_s dV_s \qquad (1)$$

where E_s is the electric field at the probe 120 produced by

15 the sample 110, P_p is the induced probe polarization density under excitation at ω_p, E_p is the electric field at the sample 110 produced by the probe 120, and P_s is the induced sample polarization density under excitation at ω_s. The interaction force associated with the interaction energy H is

20

$$\vec{F} = -\nabla H . \qquad (2)$$

Under the near-field configuration, the integrals may be dominated by volumes in the sample 110 and the probe 120

25 extending much less than one wavelength in one or more

PATENT
ATTORNEY DOCKET N⬤ 06618/457001/CIT 2986

dimensions. When the spatial extent of the interacting

regions of sample 110 and probe 120 are far smaller than one

wavelength, there is negligible cancellation of the force due

to any difference in wavevectors of the two different

5   excitation radiation waves. Hence, two or more excitation

waves may be in any directions, including being orthogonal to

each other as illustrated. The directions and polarizations

of the excitation waves may be adjusted according to the

geometrical dimensions and relative positions and orientations

10 of the sample 110 and the probe 120 to enhance the induced

polarizations P_s and P_p and their interaction.

Such optical interaction energies contribute to the

potential energy relevant to the motion of an irradiated

particle. For example, optical tweezers use the focal point

15 of a laser beam to create a potential minimum which, if

sufficiently deep, may trap the Brownian motion of an

otherwise free particle. Gordon and Ashkin, "Motion of atoms

in a radiation trap", Physical Review A 21, 1606-1617 (1980).

Novotny et al., "Theory of nanometric optical tweezers", Phys.

20 Rev. Lett. 79, 645-648 (1997), and Ashkin, "Forces of a

single-beam gradient laser trap on a dielectric sphere in the

ray optics regime", Method Cell Biol. 55, 1-27 (1998). In the

system 100 in FIG. 1, assuming that the sample 110 is fixed at

or near a surface of the holder 112 and the probe 120 is

25 suspended by a mechanical harmonic oscillator, the potential

energy function of the probe 120 determines the motion of the

- 9 -

probe, with or without excitation waves. The optical

interactions between the sample 110 and the probe 120 under

optical radiation contribute to this harmonic oscillator

potential and hence the motion of the harmonic oscillator can

5   be measured to extract information about the optical

interactions.

Under proper conditions, the interaction energy in

Equation (1) can be expanded in powers of the displacement

coordinate of the harmonic oscillator. The coefficient of the

10   linear term represents a force or torque in the limit that the

probe's oscillator coordinate is a pure translation or

rotation, respectively. In magnetic resonance, this force

(with magnetic polarization and E replaced by B) can be

experimentally demonstrated to deflect atomic beams due to the

15   known transverse Stern-Gerlach effect. The optical

counterpart is the gradient-dipole force. For example, the

phenomenon of optical tweezers uses the DC component of the

force. In the DC case, a steady-state polarization is induced

by a certain Fourier component of the incident field and the

20   spatial gradient of that same Fourier component acts to push

on the particle in proportion to that polarization.

Equation (1) can have AC components if the time

dependence of P_s includes a field at a frequency (ω_s) different

from the frequency (ω_p) of the field responsible for the field

25   gradient. This is the basis of proposals for ultrasensitive

spectroscopy of trapped ions where the AC force is at the difference between two applied rf frequencies and is matched to one of the frequencies of the trapped ion motion. U. S. Patent No. 4,982,088 to Weitekamp et al., and Pizarro and

5 Weitekamp, "Magnetic resonance of trapped ions by spin-dependent cyclotron acceleration", Bull. Magn. Reson. 14, 220-223 (1992). Another technique for magnetic resonance force microscopy creates the AC force at the Larmor frequency by spin-locking the transverse magnetization in the presence of a

10 ferromagnetic particle, which provides a static field gradient. Sidles, "Noninductive detection of single-proton magnetic-resonance", Appl. Phys. Lett. 58, 2854-2856 (1991). If either the sample or the ferromagnetic particle is bound to a cantilever with a mechanical resonance close to the Larmor

15 frequency, its harmonic motion will be resonantly driven. Related magnetic resonance methods using time-dependent longitudinal magnetization have been demonstrated and show great promise for extending spin spectroscopies to micron scale and below. Sidles, "Magnetic-resonance force

20 microscopy", Rev. Mod. Phys. 67, 249-265 (1995), Leskowitz et al., "Force-detected magnetic resonance without field gradients", Sol. St. Nucl. Magn. Reson. 11, 73-86 (1998) and "Force-detected magnetic resonance without field gradients", Bull. Am. Phys. Soc. 44, 543 (1999), and U.S. Patent

25 Application No. 08/872,528, "Force-Detected Magnetic Resonance Independent of Field Gradients" by Weitekamp et al. (to be

issued). Single-spin designs have been proposed based on audiofrequency nanoscale cantilevers with force sensitivity at a level of attonewton/(Hz)$^{1/2}$.

The system 100 shown in FIG. 1 can be operated in various

5   modes. One mode is that both the sample 110 and the probe 120 are excited by excitation radiation waves of different frequencies. Another mode is that one of the sample 110 and probe 120 is under a static electric or magnetic field while the other is illuminated by an excitation radiation wave. Yet

10   another mode is that one of the sample 110 and probe 120 has a permanent DC polarization even if no external field is applied to this permanently polarized object while the other object is applied with an external field.

The general approach in designing and operating the

15   system 100 shown in FIG. 1 is described in the following. Since the interaction force between the sample 110 and the probe 120 is essentially symmetrical, it is understood that the terms "sample 110" and "probe 120" are interchangeable if not specifically indicated.

20   A material of interest is made in a suitable size and shape as the sample. This sample is to be exposed to electromagnetic or acoustic radiation, thereby developing (in steady state) an electromagnetic polarization at the frequency or frequencies of the incident radiation and/or at sums and

25   differences of these frequencies. A frequency of the

- 12 -

radiation in the sample will be denoted ω_s. A special case is

$\omega_s = 0$, which is a static electric or magnetic polarization.

A further special case is no irradiation, in which case the

permanent (as opposed to induced) DC polarizations of the

5   sample may be studied or fluctuations in polarization may be

studied. In some embodiments, additional relevant frequencies

will be those of resonances in the electromagnetic

susceptibility of the sample or the induced susceptibility

characteristic of the irradiated sample. The sample may be

10   stationary or in an arbitrary state of motion. A special case

is that the sample itself constitutes a part of a mechanical

oscillator.

The probe mechanical oscillator may be additionally

exposed to electromagnetic or acoustic irradiation so as to

15   develop its own characteristic polarization(s) and

susceptibilities. A frequency of this second irradiation

and/or polarization is denoted by ω_p. In the special case

that the sample is part of an oscillator, then this second

irradiation may be associated with the fixed (as opposed to

20   mechanically oscillating) probe frame. This second

irradiation may then exist dominantly in free space or in a

stationary material object, extending outside that object as

evanescent and/or propagating modes. This second irradiation

may also exist predominantly in a probe mechanical oscillator,

25   even when the sample itself also comprises part of an

oscillator. The special case that $\omega_p = 0$ is of interest, since DC polarizations may be large and persist without continuing input of energy.

The sample 110 and the probe 120 should be disposed

5   relative to one another to allow the fields or vector

potentials associated with the electromagnetic polarizations

of the probe and sample volumes to interact. The relevant

interactions include all electromagnetic phenomena, including

propagating waves and evanescent waves. Oscillation of matter

10   in the sample and probe positions and/or shape will generally

be an aspect of the electromagnetic polarization and contact

sample and the probe may be in contact with each other. The

actual contact between the probe and the sample is not

necessary, since the interaction is through fields whose

15   useful reach extends well beyond the length scales (e.g., van

der Waals radii) associated with mechanical contact. This

interaction may be optimized by bringing the sample and the

probe into close proximity, typically much less than the

electromagnetic wavelengths of interest. The distribution of

20   the sample and probe material can be arranged to optimize

their force of interaction, given other constraints. The

relative orientations of the sample and the probe and of the

polarizations and momenta of the fields incident on the sample

and the probe are additional geometric variables which may be

25   used to optimize the interaction or provide information on the

sample. An aspect of this interaction is the electromagnetic

force which sample and probe volumes exert each upon the other

in proportion to the product of the polarizations in each.

Another aspect is the dissipation of the mechanical or

5   electromagnetic oscillations of sample or probe which are

enhanced by proximity of the sample and probe.

The frequencies ω_f present in the polarization-dependent

forces between the sample 110 and the probe 120 are in general

within the mechanical frequency response range of the

10   oscillator. In some applications, ω_f may be at or near the

resonance frequency of the oscillator engaged to one of the

sample or probe or the resonance frequencies of the two

mechanical oscillators to which the sample and probe are

respectively engaged. Let ω_h be the resonance frequency of

15   the harmonic oscillator whose detection will provide a measure

of the electromagnetic interaction being probed. Then the

condition of $\omega_f \approx \omega_h$ can optimally excite the oscillator

amplitude in proportion to the interaction force. In

addition, the system can be adjusted so that the force

20   frequency ω_f is a harmonic of the resonance frequency ω_h of

the oscillator. For example, the condition of $\omega_f \approx 2\omega_h$ can be

used to parametrically amplify the pre-existing amplitude of

the oscillator and/or to excite a classically-forbidden double

quantum excitation of the oscillator.

In either of the above conditions, detection of the
resulting change in amplitude can be analyzed through known
mechanics to determine the force proportional to the sample
polarization and thus to determine that polarization and/or

5   relevant geometric relationships. Detection through the
nonlinear response of the oscillator and frequency shifts of
the oscillator and damping of the oscillator are possible
alternative means of using the favorable properties of an
oscillator for force detection. This force is also usefully

10   viewed as proportional to the gradient (with respect to the
mechanical oscillator coordinate) of the field of the probe at
the sample volume. A variety of modulation schemes involving
the sample or the probe are possible in order to achieve the
mechanical resonance condition; it is only necessary that the

15   sum or difference between a frequency present in the
polarization of the probe and one present in the sample act on
the mechanical degree of freedom in a manner which can be
detected.

In the case that the system of sample and probe has two

20   or more mechanical oscillators, the resonance may be such as
to couple energy and action between two (or more) oscillators.
For example, if ω_{hs} and ω_{hp} are two harmonic oscillator
frequencies and ω_f is the frequency of an interaction between
the oscillators having a term linear in each of the oscillator

25   coordinates, then coherent oscillatory exchange of action

between the oscillators occurs at a frequency proportional to the strength of the interaction. The resonance condition at which such exchange is optimized is $\omega_f = |\omega_{hs} \pm \omega_{hp}|$.

This and other mechanisms of coupling energy and/or

5 action between oscillators may also play a role in optimizing a set of oscillators in different ways for different purposes. For example, one oscillator may have properties optimized for being driven by interaction with a specific type of electromagnetic field (characterized by frequency,

10 polarization, magnetic and electric amplitude, etc.), while another nearby oscillator is optimized for a particular method of detecting its mechanical properties. By transferring action between the first oscillator and the second oscillator by whatever means, the favorable properties of each are

15 incorporated into the measurement procedure. A related use of such exchange of action is to use the controllable amplitude of one oscillator to set the amplitude of another, which might not otherwise be accessible. This can be useful in setting an initial condition of minimum uncertainty prior to coupling an

20 oscillator to an unknown field to be measured.

In some embodiments, it may be necessary to arrange multiple instances of coupling and detection with multiple mechanical oscillators or the same oscillator successively in time. The results of these separate measurements may then be

25 combined mathematically, for example, to form desired

correlation functions. As an example, the product of two

similar and simultaneous measurements with probe oscillators

separated in space can be used to measure the second order

correlation function of the electromagnetic quantity measured,

5   such as the near field of an electromagnetically polarized

sample of interest.

Measurements may be made by repetitively adjusting a

variable to record the displacement of the oscillator or other

mechanical observable as a function of the variable.

10   Variation of frequency, amplitude, momentum, or polarization

of one or more of the incident fields would provide

spectroscopic information. Increment of a time variable in

some sequence of irradiation of the sample will encode dynamic

information such as Bohr frequencies or relaxation times in

15   analogy to time-domain spectroscopic measurements. Variation

of the relative orientation of the various fields and objects

provides additional information, including polarization

information.

Imaging of an extended sample can be achieved by varying

20   the position of the probe relative to the sample. Imaging of

the second-order correlation function of the electromagnetic

field of the sample can be performed by repeated measurements

of the product of the displacement of two probe oscillators as

a function of the positions of these probes. Variation of the

25   sample properties by a change in thermodynamic state, chemical

composition, or additional prior irradiation, provides a

method for recording information with high spatial and

frequency resolution. Advantages of such data recording

include enhancing bit density, lowering recording energy, and

accelerating read and write rates due to its sensitivity to

5   small polarizations or changes in polarization, its spatial

resolution, its compactness, its convenience and its potential

for massively parallel implementation.

When the system is operated at $\omega_f = |\omega_p - \omega_s|$, special

operating advantages can be achieved. For example, as

10   suggested above, constant amplitude irradiation of sample and

probe volumes at frequencies which differ by approximately a

resonant frequency of the mechanical oscillator will allow

detection of the sample's polarization by way of the

displacement of the oscillator. This illustrates the

15   possibility of realizing forces at practical mechanical

frequencies from polarizations at much higher frequencies for

example optical frequencies. Since it is advantageous for ω_f

to be maintained in a narrow range of frequencies in order to

efficiently and reproducibly drive the mechanical oscillator,

20   it will often be useful to generate the fields responsible for

driving the polarizations in the sample and the probe from the

same radiation source by modulating its output to produce

excitation waves at different frequencies. Such methods have

the property that the resulting force of interest can be as

25   stable as the modulation or shift frequency and is

substantially insensitive to fluctuations in the frequency of

the original source.   For example, an amplitude modulation of

a source at $|\omega_p - \omega_s|/2$ generates sidebands with a separation of

$|\omega_p - \omega_s|$ in frequency, independent of the initial spectrum.

5   Another example is the use of diffraction by a traveling or

standing wave in refractive index to both diffract and shift

the frequency of an electromagnetic beam (by that of the

diffracting wave), thereby providing spatially separated, but

mutually coherent, beams for use in sample and probe volumes.

10   The frequency ω_h of the mechanical oscillator in general

may be a function of temperature, of the applied fields and of

its position with respect to the sample.   Thus, it is

desirable to have an observable whose observation can be used

in a feedback loop to maintain the mechanical resonance.   The

15   derivative of the oscillator's amplitude with respect to ω_f

may be used as such an observable.   This derivative is

minimized at the mechanical resonance. It could be

conveniently measured by modulating ω_f at a frequency ω_{mod},

e.g., in a sinusoidal manner, over a range small compared to

20   the width of the mechanical resonance and observing the

sidebands at $\omega_{f0} \pm \omega_{mod}$ in the oscillator motion. Here ω_{f0} is

the center of the range of modulation.   These sidebands vanish

only when $\omega_{f0} = \omega_h$, so the amplitude of a sideband provides the

error signal in a feedback loop.   Either ω_{f0} or ω_h can be

25   adjusted to maintain the null of this error signal.   The

former is simply a parameter of the incident fields and can be

adjusted electronically. The latter can be adjusted through

the value of additional quasi-static forces on the oscillator

of an elastic, optical, capacitive, or magnetic nature. For

5   example, controlling the temperature of the oscillator may

generally change its elastic force constant, providing a

convenient way of varying ω_h. Such feedback schemes can occur

simultaneously or interspersed with the scanning of position

needed for imaging or the scanning of optical frequency needed

10   for spectroscopy.

Particularly in scanning probe embodiments of the

invention, it may be desirable in certain applications to have

independent control over the measurement of the distance of

the probe tip from the sample surface, whose topography is

15   generally unknown. The combination of the present method with

known scanning probe methods can be used to achieve this goal.

This combination could take the form of coordinating the

movements of separate scanning probes for the different

functions.

20   Alternatively, the same probe may be operated to

incorporate multiple methods to perform the desired

measurements. For example, atomic-force microscopy (AFM)

makes use of DC displacements of cantilevers into or onto or

adjacent to which the optically driven mechanical oscillator

25   of the present FDOS invention could be placed. The contact

with the sample would take place in the usual manner of the various AFM methods, while the position of the FDOS tip relative to the sample would be controlled and measured by virtue of its known (fixed) relationship to the AFM tip.

5   Analogously FDOS could be combined with scanning tunneling microscopy, near-field scanning optical microscopy, and other scanning probe methods.

Applications Using Dissipative Optical Forces

10   The above examples deal with the elastic part of the interaction force between the sample and the probe. However, the dissipative part of the force between the sample and the probe may also be used for measurements. This is achieved, for example, by using the rotating-frame (or dressed-state)

15   transitions to couple high-frequency polarization in the sample to lower-frequency polarization in the probe. More specifically, a ferroelectric or paraelectric probe oscillating at ω_h can experience increased mechanical dissipation when the Rabi frequency associated with the

20   interaction of the electromagnetic radiation in the sample with a spectroscopic transition of the sample matches the oscillator frequency ω_h. This dissipation may be viewed as the result of the changing electric field of the probe at a position in the sample driving low frequency transitions of

25   the sample that exist by virtue of the AC polarization of the

- 22 -

sample. The analog of this process for a magnetic-dipole allowed transition and a ferromagnetic probe is another example. This is a distinct method of converting a high frequency spectroscopic interaction in the sample to a

5 mechanically detectable interaction at ω_h.

Another variant of the method that may result in detectable optically-induced dissipation of the oscillator motion involves the application of the single incident optical field on the probe, which again can be referred to by its

10 frequency ω_p. The motion of the oscillator (thermal or driven in any way) can be used to cause a modulation on the (near) field and hence can introduce Fourier components at or near ω_p $\pm \omega_h$. The absorption of either of these sidebands by the sample involves an exchange of energy with the oscillator, as

15 well as with the incident field. Such energy exchange could be detected by a change in its motion.

Detection of the Oscillator Motion

The harmonic displacement of the oscillators in general

20 may be measured by a number of techniques for measuring small displacements, including but not limited, capacitive detection, optical levers, and electron tunnel sensors. It is discovered that the motion of the oscillator can also be measured by monitoring quasi-elastic scattering of light.

This technique may be combined with other motion-detection techniques.

It is widely believed that picometer motions of nanoscale objects are too small to be reliably observed. Some optical measurements of displacement by quasi-elastic scattering use a mirror with an area much greater than λ^2 to specularly reflect the light in a Fabry-Perot interferometer. This relatively large area was maintained even in applications where other advantages of small size were appreciated, because it was understood to be necessary. This restriction to large areas, as needed for specular reflection, leads to oscillators with mass that is far greater than is optimal for the detection of weak forces. Much smaller nanoscale oscillators have been fabricated as components of ultrasensitive sensors, but their displacements were measured using electrons. Oscillation of carbon nanotubes has been observed by imaging the time-average trajectory with an electron microscope, a method that has the disadvantage of being insensitive to the phase of the oscillator. The carbon nanotubes with metallic particles at their tip used in these studies is one example of suitable nanoscale oscillators. Because of their robustness, small motional mass, and the demonstrated possibility of bonding other materials to them, carbon nanotubes are a particularly possibility for the oscillators and other small parts needed for the present inventions.

Phase sensitive electrical methods have been demonstrated on nanoscale oscillators that required current paths on the oscillator which are displaced by the oscillator motion. This work illustrates the existence of fabrication methods for

5   making nanoscale semiconductor oscillators with attached metal parts, as is needed for the embodiments of the present invention. The present optical detection method is advantageous in not requiring conducting paths, thus eliminating a difficult fabrication step and reducing the

10   oscillator damping associated with extended surface layers of conductor. In addition, the noise associated with shot noise and feedback forces for photons can be lower than that practical with electrons.

Thus the optical detection method of the present

15   invention is generally applicable to nanoscale oscillators. At least part of the oscillator can be made from materials which scatter light effectively. For metals, this scattering can exceed that which would be estimated by extrapolation from bulk optical properties, due to the plasmon resonances of

20   nanoscale metal particles. These resonances are used here to detect the motion of nanoscale oscillators. It includes the extension of quasi-elastic light scattering from the well-known case of harmonically bound mirrors to objects so small that they may even scatter essentially isotropically.

Such scattering is somewhat analogous to stimulated Raman scattering associated with the natural vibrational modes of molecules, which are highly anharmonic oscillators. It is an aspect of the present invention that the oscillators are

5   engineered compositions of matter with essentially harmonic vibrations and large Raman cross sections. The physical mechanisms contributing to the large observed cross section may include the phase modulation of the scattered field by the motion of the oscillator through space, the amplitude

10   modulation by the oscillator motion of its own optical frequency polarization through gradient fields at its location, the amplitude modulation of the optical polarization of surrounding objects by the changing field of the moving oscillator at those surrounding objects. It is also

15   recognized that the oscillator and surrounding objects can jointly determine the frequency of plasmon or other electronic resonances and that their relative displacement by the oscillator motion will change the frequency of this resonance. If ω_d is on the slope of that resonance, then the changing

20   frequency of the resonance will appear as an amplitude modulation, providing another mechanism of enhancing the scattering at $\omega_d \pm \omega_f$. Polarization modulation by an oscillator motion that has a torsional component can similarly be used to create such sidebands, which would be detected by

using a polarizer to detect the photocurrent of one

polarization component of the scattered field.

The non-specular nature of the light scattering reduces

the fractional efficiency f with which the scattered light is

5   collected. It is desirable to keep this efficiency

sufficiently high that the uncertainty associated with the

detection of the scattering does not become an important

source of the overall noise. It is well known that lenses can

be used to effectively collimate or focus light originating

10   from a point-like source. In addition waveguides may be

positioned so that a large fraction of the light of the point

source enters a guide mode or modes of the waveguide. In

these ways, even isotropically scattered light can be brought

to the detector with adequate efficiency. This scattered

15   light will generally contain elastically scattered light at

ω_d, as well as the quasi-elastically scattered light at $\omega_d \pm \omega_f$

which constitutes the optical signal. The interference of

these mutually coherent waves at the detector creates a

component of the photocurrent at ω_f proportional to the

20   amplitude of the oscillator, which constitutes the electrical

signal.

In general, a polarizer is advisable in the detection

path, since, together with lenses, it also aids in

discriminating against light that has not taken substantially

25   the same path as that at $\omega_d \pm \omega_f$ and would thus not interfere

coherently with it. Such discrimination is desirable to

minimize both shot noise and the necessary dynamic range of

the detection system. Another approach to minimizing the

necessary dynamic range of the detection system is to use

5   destructive interference of mutually coherent beams at ω_d, one

of which also contains the quasi-elastically scattered

sidebands, so that in the absence of oscillator motion the

photocurrent is near a null.

There are a number of applications of nanoscale

10   oscillators that would benefit from the present highly

sensitive optical method of detection. In applications such

as force-detection, calorimetry, viscous damping, and

measurement of the oscillator's mass (e.g. to detect binding

of a molecule as additional mass) sensitivity improves as the

15   oscillator is reduced in size and as its ring down time is

lengthened. The present optical method and the oscillator

design features (such as using the plasmon resonances of metal

nanoparticles attached to the oscillator) enables the

extension of these methods to smaller sizes and longer ring

20   down times than would be practical with prior art detection

methods of nanoscale oscillator displacements.

Applications Involving Extended Oscillators

The present techniques can also be applicable when sample

25   and probe volumes are in close proximity over extended lengths

or areas that are greater than the wavelengths of interest.

Suppose that a single oscillator extends in one or two

dimensions over a distance comparable to or greater than the

incident wavelengths. The interaction with a similarly

5   extended sample in its near field along the third dimension

will still be constructive, so long as the inverse of the

difference in wavevectors of the incident fields is small

compared to the inverse of the oscillator dimension parallel

to it. Thus, for example, the pixel size in force-detected

10   optical microscopy need not be much shorter than a wavelength.

Using such large oscillators could simplify fabrication. It

may also increase signal-to-noise ratio for each device.

Application of Oscillator Arrays as A Nonlinear Optical Medium

15   The present mechanisms of driving and detecting the

motion of individual oscillators are also applicable to arrays

of oscillators in one, two, or three dimensions. The goal may

be simultaneous imaging or spectroscopy over a line, a plane,

or a volume to achieve greater throughput. As an example, a

20   surface could be imaged by a two dimensional array of FDOS

oscillators acting simultaneously. Since it may be desirable

to avoid having separate detectors for each oscillator, one

embodiment may use a single optical detector to collect and

measure the scattered light from a group of oscillators as a

25   composite signal. If it is possible to selectively modulate

(e.g. turn off) the signal from each oscillator, then the contribution of each oscillator to the total signal may be determined by taking linear combinations of composite signals with different sets of oscillators so modulated.

5   An efficient strategy for obtaining and sorting out a large set of such distinct composite signals is based on the Hademard matrices, a linearly independent set of matrices each element of which is zero (off) or one (on). The elements of these matrices are assigned in one-to-one correspondence with

10   each oscillator. A set of measurements is made, with each oscillator turned on or off according to the corresponding element of a different Hademard matrix. The Hademard transform deconvolves from this signal the signal from each oscillator, with the assumption that it contributed identically in each

15   measurement in which it was on. Thus this transformed data set is an image of the underlying surface, or more generally of the environment of the oscillators, with each oscillator contributing a pixel.

       The states indicated as on and off might differ only in

20   the distance between the probe and the sample, controlled, for example, by piezoelectric or thermal expansion of the probe dimension perpendicular to the surface. Note that this same strategy could be used in cases where the detection did not involve an optically driven mechanical oscillator, but some

25   other means of spectroscopy relying on near field enhancement. Both apertureless near-field scanning optical microscopy and

surface-enhanced Raman spectroscopy are examples where the

signal is light scattered by the surface species of interest

enhanced by the presence of a nanoscale tip. Hademard

transform versions of these methods would be advantageous in

extending them to linear or planar arrays of probes, thereby

increasing sensitivity and throughput, while retaining spatial

resolution.

The set of pixels comprising the "image" of the surface

might have been written as a form of data storage. The method

10   of this writing may involve objects distinct form those used

in the detection strategy. It is known that tips with

nanoscale radii of curvature can be used to make nanoscale

indentations in various media. The force of indentation can

be mechanical or can be due to rapid thermal expansion of the

15   tip. It is also possible (and suspected in some cases) that

the enhancement of optical fields near nanoscale tips can lead

to damage even without physical contact. The tip used in

writing could be the same as that used as the detection probe

(e.g., oscillator) or could be separately optimized for the

20   writing process. Note that in both the writing and the

reading steps, the data density (or image resolution) is not

limited by the spacing of the read or write tips, but rather

can be increased by moving the array relative to the substrate

and repeating the read and write steps at resolvable

25   locations.

Noting that the oscillator array plays the role of a nonlinear optical medium, analogs of various applications of nonlinear media are possible. In particular note that the overall process of FDOS can be viewed as four-wave mixing with

5 the fourth wave being the quasi-elastic scattering. For example, in analogy to so-called coherent anti-Stokes Raman scattering, the scattered light contains the frequency $\omega_s - \omega_p + \omega_d$. Momentum matching conditions are also analogous. Thus, the overall process multiplies wavefronts. This is the

10 basis of methods of optical computing and pattern recognition. Similarly phase conjugate mirrors might be made from this new composition of matter, arrays of mechanical oscillators (including the part of the array playing the role of "sample") with intense optical interactions and strong coupling of that

15 interaction to the mechanical motion through engineered gradient dipole forces. The wave mixing can also be used to produce a wave-mixing signal at $|\omega_p - \omega_s| \pm \omega_p$ when the probe-sample are driven by coherent radiation waves at ω_s and ω_p, with or without the detection wave at ω_d. The amplitude of

20 the wave-mixing signal is essentially proportional to the amplitude of the mechanical motion of the oscillator.

Holography is another way in which information can be written and read from areas or volumes of nonlinear media with dimensions much greater than the optical wavelength. Since

25 the present oscillators are optically driven and read, any

such scheme is adaptable to them. For example, the write step could entail mechanical damage done to a substrate that is contacted only when the oscillator at that position is strongly driven. This driving can be made to depend on

5   position by using interfering waves of different wavevectors at each of the frequencies ω_p and ω_s that drive the oscillator. Many optical writing schemes are also relevant in combination with FDOS as the read method.

Reading permanently-stored data with FDOS can be

10   subdivided into two steps which may take place sequentially or coincidently in time. The first step is to transfer the written information to the oscillator motion in preparation for reading. This transfer step would take advantage of the difference in oscillator amplitude that results from the

15   change in state of the substrate done by the write step with the substrate near each oscillator serving as the "sample". By using sufficiently low power or different wavelengths than in the write step, the transfer step could be made substantially nondestructive. The second step, which may occur

20   simultaneously or subsequently to the transfer step, is to scatter light off the driven oscillator array to read the information. Each step benefits from the well-known holographic strategies. In particular, information can be written to or read from different stored grating vectors

25   simultaneously due to the inequivalence of different

directions of the incident and scattered light. Also

inhomogeneous broadening of the spectroscopic transitions and

photochemical or nonphotochemical hole burning can be

exploited by using different frequencies to write and read

5   different subsets of molecules or crystal sites, thereby

increasing data density and throughput.

The mechanical nature of the oscillator array allows

induced shifts of ω_h to also play the role of storing

information. For example, if the oscillator and its support

10   contained magnetic material, then changing the magnitude or

relative direction of their magnetic moments would change the

magnetic contribution to the oscillator restoring force and

shift ω_h. Alternatively, the change in this frequency with the

approach of a magnetic body could provide the information on

15   the magnetic moment of the oscillator or the other body.

Methods for writing such magnetic bits are highly developed

and include magnetic write heads and optically induced

temperature changes. The present method provides a new way of

reading these changes and does not rely on directly measuring

20   the magnetic field per se. The optical aspect of the reading,

including holographic versions, could provide advantages.

The application of the present techniques includes

special cases where the relevant mechanical degrees of freedom

are overdamped, so that no well-defined oscillator frequency

25   is definable. For example, the mechanical response of

molecules can involve translations against viscous forces. The attractive interaction between a molecule and an irradiated nanoparticle has applications in the separation technology. See, e.g., Novotny et al., "Theory of nanometric optical

5   tweezers", Phys. Rev. Lett. 79, 645-648 (1997). One key idea is that the attractive potential between a dissolved molecule and the near field of stationary irradiated nanostructures will impede the flow of the former past the latter. An analogy is affinity chromatography, where the forces are those

10 of weak, transient chemical bonds. Here the forces applied could have the specificity of spectroscopic signatures, so they will allow separations that might not be practical on the basis of other properties. Unlike some other separation techniques using light fields to create translational forces

15 on molecules and particles, this embodiment of the present separation technique uses the differences in the polarization between fixed and mobile phases and/or the use of evanescent fields. In particular, the use of evanescent fields increases the magnitudes of the interaction forces to a practical range

20 for separation in fluids, where the frequent collisions and relatively high temperature impede long-term trapping or acceleration by optical forces.

Another example is the case of mechanical oscillators, each comparable to or small compared with the wavelength of a

25 relevant electromagnetic mode and grouped together in an array extending in one or more dimensions over a distance that is

comparable or large compared to one wavelength of the

radiation waves. The positions of the oscillators may then be

chosen so as to interact constructively with one or more

electromagnetic modes. An analogy is to the use of layering of

5   materials of different refractive index to create gratings,

lenses, holograms, and related arrays which scatter light in a

desired fashion. The oscillators of the present invention,

together with the nearby "sample" material may similarly be

arrayed in a systematic fashion to make analogous use of their

10   novel optical properties. In particular, it is the nonlinear

refractive index that is enhanced.

As an example, the exchange of energy between two optical

frequency modes would be enhanced when a wavevector of the

distribution of amplitude of the mechanical oscillators

15   matches the difference in wavevectors of the electromagnetic

modes in question. For example, the two optical modes in

question could be surface plasmons localized in the same or

opposite surfaces of a plane containing the (ferroelectric)

oscillators.

20   In addition to building in such a difference wavevector,

it could be optically-induced in an array of oscillators and

samples, whose distribution of positions may be arbitrary. The

difference of the wavevectors of the two incident waves whose

difference frequency is resonant with the oscillator becomes

25   the wavevector describing the variation in the phase of the

oscillator motion as a function of position in the array. Such

an arrangement would allow the state of motion of the array of

oscillators to be set and read out in analogy to stimulated

Raman spectroscopy of molecular vibrations or crystal phonons,

but with the artificial mechanical oscillators replacing the

5   naturally occurring oscillators of a particular material.

This method of addressing an array can be utilized to allow

massively parallel implementation of any of the applications

described herein in terms of individual oscillators or small

localized groups of oscillators. Variation of the k vectors

10   coupled by the mechanical oscillators would allow different

linear combinations of the oscillator amplitudes to be set

and/or probed.

FIG. 3 shows one implementation of the system 100 shown

in FIG. 1. A sample 310 is placed on a XYZ-scanner 312 under

15   a control of a control module 360. A probe 320 is engaged to

a mechanical oscillator 322. A single radiation source 301,

e.g., a tunable laser, is used to generate the sample and

probe excitation waves. A frequency-shifting device 303,

e.g., an acousto-optical modulator, is used to modulate the

20   output laser from the laser 301 to produce a sample excitation

wave at ω_s and a probe excitation wave at ω_p. The amplitude

and polarization of each excitation wave can be independently

controlled by using a control optical module 305 with

attenuators and polarizers before being combined as a beam 307

25   to illuminate the sample and the probe. The AO modulator can

operate in the frequency range from about 100MHz to about 600MHz of the mechanical oscillator 322 so that the difference between ω_s and ω_p is within the response range of the oscillator 322.

5   The displacement of the probe 320 due to the sample-probe interaction can be measured by a non-invasive technique based on measurement of the scattering by the probe 302 of a detection wave at a frequency ω_d. A laser 330 may be positioned to produce the detection wave. The scattered

10 detection wave from the probe 320 is collected by a lens system 322 and received by a photodetector 334. A RF spectrometer 350 and a computer 352 are used to process the detected photocurrent. The interference between elastic and quasi-elastic scattered light is detected to extract the phase

15 change due to the motion of the probe 320 to produce a photocurrent at the oscillating frequency ω_h of the oscillator 322. This is conceptually related to the observation of harmonic oscillator probes in AFM and force-detected magnetic resonance, where the Brownian motion limit (down to ~

20 pm/$(Hz)^{1/2}$) has been reached for audiofrequency oscillators ranging from μm to micron width. Rugar et al., "Improved fiber-optic interferometer for atomic force microscopy", Appl. Phys. Lett. 55, 2588-2590 (1989) and Walters et al., "Elastic strain of freely suspended single-wall carbon nanotube ropes",

25 Appl. Phys. Lett. 74, 3803-3805 (1999).

In the present embodiment, the far field light at frequencies $\omega_d \pm \omega_h$, may be viewed as coherent (or stimulated) Raman scattering, the nanoscale analog of reflection from an oscillating mirror. The amplitude of the field at these

5 sideband frequencies is due to the motional modulation of the phase, polarization and/or amplitude of the coherently driven dipole at ω_d. Proper selection of the design parameters can make the photon shot noise small compared to Brownian motion at room temperature. The other quantum noise source

10 associated with the scattering is the back action on the oscillator of the uncertainty of the change in photon momentum. These photon pressure fluctuations are a negligible noise contribution relative to both Brownian motion and shot noise for the range of design parameters.

15 The operating frequency range of 100~600 MHz of this embodiment is high enough that room-temperature thermal displacements and driven displacements are a small fraction of the oscillator dimensions, thus ensuring harmonic motion without the need for cooling or feedback. Meanwhile, these

20 frequencies are also low enough that these displacements are optically detectable.

The polarizations at frequencies other than ω_s and ω_p generally do not interfere with the detection. Cross terms between polarization components at identical frequencies in

25 sample and probe produce a DC force on the oscillator and

forces at the sum of the optical frequencies. The DC force

gives rise to a displacement of the oscillator that is smaller

than the resonant signal by a factor equal to the mechanical

quality factor of the oscillator, $Q_h = \tau_h/\omega_h$, where τ_h is the

5   decay time for free oscillation. This shift of the

oscillator's equilibrium position will be vastly smaller than

the resonant displacements of interest, since by design $Q_h \gg 1$.

Sum-frequency forces are even less effective at disturbing the

oscillator, since they are vastly higher than any mechanical

10   frequency.

In general, sources of radiation at ω_s could in principle

drive the probe oscillator through its polarization, even in

the absence of the targeted feature of the sample. This

creates a background analogous to that in many coherent

15   spectroscopic measurements of condensed matter. However, the

present technique allows for the reduction of the effects of

this background contribution because the background driving

essentially vanishes for a plane wave and, more generally,

whenever the net effect of sources other than the target

20   feature create no gradient along the harmonic oscillator

coordinate at the probe position. For example, as shown in

FIG. 2, the harmonic oscillator coordinate can be chosen to be

in a plane parallel to that of the substrate, making it

insensitive to the larger gradients normal to the substrate.

25   Similarly, the signal torque on a torsional oscillator can be

made proportional to a field component which is orthogonal to

the background fields, but which appears in the field due to a

nearby point dipole. When a probe-oscillator system is

designed to have two or more fundamental modes, these multiple

5   modes provide distinct information at a given probe-to-sample

coordinate and may be resolved by their separate frequencies.

The driven oscillator displacement is to a good

approximation a linear response to the near-resonant force. At

a particular frequency that response can be decomposed into

10   components that are in-phase or 90 degrees out of phase with a

reference wave at that frequency. Alternatively, the

oscillator amplitude can be viewed as a complex number whose

real and imaginary parts are these two distinct components.

Signal proportional to these two components are simultaneously

15   available by standard methods of phase sensitive detection of

the electrical signal in the detection module 103 proportional

to the oscillator amplitude.

This is a convenient viewpoint from which to discuss

interference effects between the various sources of such

20   forces. For example, the complex signal as a function of the

scanned frequency ω_s in a spectroscopic application will

reveal the complex lineshape which is understood from existing

theory to characterize the complex susceptibility associated

with the pairs of levels connected by that scanned incident

25   field. Interference effects between simultaneously

- 41 -

contributing parts of the sample have, in addition to these well known spectroscopic phase relationships, geometric information, since the phase of the force from each sample element depends also on its position relative to the probe.

5   Scanning of the probe over the sample reveals the image at the "color" of the frequency ω_s. Combining observations from different normal modes of the probe coupled to the oscillator, distinguished by ω_h, or from different probe geometries, provides the phase and direction of the target's

10   optical response at each ω_s and each resolvable pixel, the size of which will be at least as small as existing NSOM methods. When a probe-oscillator system is designed to have two nominally degenerate fundamental modes, that in practice will be split in frequency by any (intentional) asymmetry,

15   thus providing distinct information at a given probe-to-sample coordinate.

Cases may arise where background signals, due for example to substrate roughness, create a dynamic range problem if large compared to the single-molecule signal of interest. Such

20   background can be further mitigated by using frequency modulation strategies developed in absorption spectroscopy. For example, if the frequency of the common source from which ω_s and ω_p are generated is modulated at ω_m so that ω_s sweeps cyclically over a fraction of the spectroscopic line of

25   interest, then the contribution to the force from the sample,

but not from the background effect, is substantially moved to $|\omega_p - \omega_s| \pm \omega_m$, one of which sidebands can be tuned to ω_h. Then the force measured is proportional to the slope with respect to frequency of the linear optical response. Scanning the center frequency of the common source gives the derivative mode spectrum of this response, suppressing the background component. Note that even if the probe were fixed or its amplitude of vibration was not substantially driven by interaction with the sample, the use of such frequency modulation scheme would be valuable in creating sidebands on the elastically scattered light. This could be described as the combination of frequency modulation absorption spectroscopy and apertureless near field scanning optical microscopy. This apparently novel experiment, though logically distinct from FDOS, could be performed with a subset of the apparatus described and is a distinct aspect of the present invention.

For each implementation of the present technique using frequency modulation of the incident light, there is an analogous one using polarization modulation. Because the induced optical polarization of matter depends on the inner product of the transition dipole and the polarization vector of the incident light, the modulation of that polarization vector modulates the source of the near and far fields of interest adding sidebands at multiples of the modulation

frequency. The polarization vector of the incident light can

be described by a three-component vector including the

possibilities of linear and circular polarization and various

admixtures. Appropriate polarization modulation schemes, in

5   the context of the present inventions, would then provide

novel methods for measuring, for example, linear and circular

dichroism.

Another possible class of resonant mechanical

displacements could come from a difference frequency

10   polarization of the probe proportional to its second order

nonlinear optical susceptibility and the amplitude of the two

incident optical fields. The interaction of this moment with

a hypothetical local DC electric field gradient across the

oscillator could drive it in the absence of a sample. This

15   may be readily avoided by minimizing the second-order optical

susceptibility by choice of materials (it is zero in

centrosymmetric objects) or minimizing the resulting moment in

the probe by choice of incident polarization directions. If

necessary, it can be further reduced by minimizing the

20   relevant component of the DC electric field gradient tensor

across the probe region. This potential artifact could also be

viewed as an opportunity; by mounting some material of

interest on an oscillator and intentionally creating an

electric field gradient, its second order susceptibility

25   tensor could be measured in an easily quantified fashion. A

related effect is that the presence of the two incident fields

- 44 -

in the sample acting through the second-order susceptibility

of the sample could create an electric polarization at the

difference frequency with a corresponding field gradient at

the probe which would create a resonant force on the

5   oscillator in proportion to its permanent electric moment,

which again is zero for centrosymmetric objects. Again, this

effect is of higher order and can be minimized or

intentionally exploited.

Note that even in the absence of the sample, the mode of

10   the incident radiation field at ω_s could in principle drive the

probe oscillator through its polarization. This background

effect vanishes for a plane wave, since it is proportional to

the spatial gradients of the field along the oscillator

coordinate. Thus it is of concern only when interaction with

15   matter has reshaped the field. Such interaction is the nature

of the signal, so the concern is background signals due to the

substrate that might create a dynamic range problem if large

compared to the signal of interest. This problem is common to

any form of spectroscopy and solutions used in other contexts

20   are applicable here. For example, mounting molecules of

interest on substrates with optical dielectric constant near

unity at the wavelengths of interest will be applicable in

some situations. A more general solution is to develop the

analogs of various modulation and nonlinear optical methods

25   that are used to separate the spectrum of interest from

background responses which vary more slowly with frequency.

For example, if the frequency of the common source from which

ω_s and ω_p are generated is modulated at ω_m so that ω_s sweeps

cyclically over a fraction of the spectroscopic line of

5   interest, then the contribution to the force from the sample,

but not from the background effect, is substantially moved to

$|\omega_p - \omega_s| \pm \omega_m$, one of which sidebands can be tuned to ω_h. Thus

the force measured is proportional to the slope with respect

to frequency of the linear optical response. Scanning the

10   center frequency of the common source gives the derivative

mode spectrum of this response, which has a lower fractional

background component.

Other approaches to limiting the background are possible

which have no analog in conventional spectroscopy, but rather

15   are unique to force detection. For example, forces on the

probe, even if resonant, will not appreciably drive the

oscillator if they are orthogonal to the oscillator

coordinate. Similarly, the oscillator could be designed and

oriented so that torques due to target material contribute to

20   the motion, while those due to background fields are in

orthogonal directions.

The signal force can be evaluated for linear optical

response of both the probe and sample. The optical near field

of metallic nanoparticles has been shown as substantially

25   consistent with the classic picture of uniform optical

polarization density modeled as the collective "plasmon"

response of the conduction electrons to the incident fields.

A significant feature in the frequency dependence of

absorption and elastic scattering cross sections are shape and

5   size dependent resonances. Inhomogeneity of particle size and

shape broaden the resonances observed on ensembles. This

limits the peak response, that is possible only for a

sufficiently homogeneous ensemble or a single particle.

Single particle studies are needed both for incisive

10   comparison of experiment and theory and to find, for example

by combinatorial synthesis, the recipe for a particle with a

narrow resonance at a particular frequency. The rf/optical

spectrometer proposed will have the bandwidth to

simultaneously observe many oscillators at once, for high

15   throughput searches. Such oscillators may be thermally

driven. Both the fabrication and optical detection methods

proposed are aimed at this problem, which is central to the

use of both metallic and semiconductor nanoparticles in any

optical application. In the examples, the near fields at ω_p

20   are not assumed to be at the plasmon resonance, and so a

relatively flat spectrometer response will apply over much of

the potential FDOS spectrum. Using such resonances may enhance

the sensitivity about another order of magnitude, assuming

accepted values of plasmon damping. Note that FDOS is itself

25   the highest sensitivity way to experimentally explore the

dependence of these resonances on the material composition, surfaces, and particle shapes.

The steady-state response to the optical Bloch equations for an individual spectroscopic transition is used to model

5   its contribution to the signal dipole $<\mu_s>$. The resonant force on the oscillator is obtained by taking the derivative of the interaction energy H according to Equation (2) with respect to the oscillator coordinate. In the limit of a point dipole sample polarization, (e.g. a single chromophore), the

10   force is $<\mu_s>G_{psh}$, where G_{psh} is the derivative with respect to the oscillator coordinate of that component of the near field of the probe at ω_p which is in the direction of the transition dipole. In the single- molecule examples, it is evaluated at the location of a chromophore 3 nm from the probe tip surface.

15   The expectation value $<\mu_s>$ can be driven to about 0.1 of the transition's dipole matrix element at the point when nonlinearity and power broadening of the response becomes appreciable. This corresponds to an average fractional excited state population of 2.5 x 10^{-3}. An incident intensity of

20    $50W/(mm)^2$ incident on a typical transition dipole of 1 debye $(=10^{-18}$ esu cm = 3 x 10^{-30} C m) will allow a 0.1 debye steady-state signal if the off-diagonal relaxation time T2 is at least 500 fs. Thus, a wide variety of electronic, vibronic, and vibrational transitions in room-temperature solids will

25   give optimized signals. This assumes a geometry shown in

FIG.2 in which there is no near field enhancement of the field

at ω_s.   Employing such enhancement could extend this optimum

response to shorter T2 at the same incident power, or allow

lower incident power at ω_s.   For example, the sample molecules

5   could themselves be mounted on metallic nanoparticles to

achieve such enhancement.

The potential for sensitivity to individual molecules

enables additional applications where the probe tip itself

would feature a chromophore molecule. This molecule would play

10   the role of the sample in the previous discussions.   The

information of interest would be the environment of this

molecule which would be altered by scanning the position of

the probe relative to surfaces or other objects. A great

variety of phenomena could be probed at molecular length

15   scales in this way, since the spectroscopy of the molecule at

the tip and its location relative to the probe would be

sensitive to electric and magnetic fields and to bonding

interactions with nearby molecules.   This strategy, where the

nominal "sample" is a static part of the probe structure, also

20   figures in many of those embodiments described herein where

arrays of such oscillators are used. In particular the use of

metallic and semiconductor nanostructures, often called

quantum dots, as both probe and sample will lead to

particularly strong optically induced forces and thus to

25   favorable sensitivity to small environmental effects.

The 0.1 debye signal used in the calculation need not

arise from a single molecular transition, but could also be

the integrated polarization of a weak or weakly driven

transition over the effectively sampled volume of some cubic

5   nanometers. For transition dipoles perpendicular to the local

direction of $E(\omega_p)$, the probe frequency ω_p may overlap with

the target absorption spectrum and yet P_s at that locus will

be controlled by the amplitude, polarization and frequency of

$E(\omega_s)$ alone. Complete imaging models all fitting the signals

10   as a function of incident polarizations, transition dipole

orientation, probe geometry and probe position will be

developed under the proposal.

A similar 50 mW/(mm)^2 maximum intensity will be assumed

at ω_p. This condition will cause negligible (< 1 degree)

15   heating of the Au/Si oscillator in the room-temperature

designs proposed, so long as the material supporting the

oscillator has a heat conductivity comparable to Si and does

not itself heat appreciably. This can be ensured by keeping

the wavelengths which are incident on any Si of micron

20   thickness above about 1100 nm or reducing the power when it is

desired to work toward the blue. Since the latter approach

would reduce the signal at shorter wavelengths, a preferable

design for the visible region is to keep all the Si in the

irradiated region as thin as possible and in contact, except

25   along the length of the oscillator, with a transparent

substrate with good heat conductivity. Methods of FDOS

oscillator fabrication which achieve this construction, e.g.,

by putting nanoscale Si or carbon nanotube oscillators on high

bandgap materials are possible. For example, CaF2 is

5   transparent well into the UV and is lattice matched to Si

within 1% at room temperature. Methods for growing carbon

nanotubes at defined positions have been described and these

are currently used as AFM probe tips. Another possibility is

to make the beams themselves from high bandgap materials.

10   Another possible approach to lowering the incident power at ω_p

and/or ω_s is by incorporating additional metallic

nanostructures so that the high intensity regions of both

fields are localized near the sample and probe.

For a signal originating from a volume smaller than a few

15   cubic nanometers, the integral over the sample volumes in

Equation (1) can be replaced by this volume element with

induced optical dipole $\langle\mu_s\rangle$. The corresponding gradient

dipole force acting between sample and probe is then found by

multiplying $\langle\mu_s\rangle$ by the gradient G_{phs} (along the mechanical

20   coordinate) of that near field component of the oscillating

probe which is in the direction of the transition dipole. The

principal noise force will be that due to the Brownian motion

of the probe harmonic oscillator. Dividing that noise force

into the gradient dipole force gives the FDOS signal-to-noise

25   ratio for measurement time t_m as

$$\text{SNR} = \langle\mu_s\rangle \, G_{phs} \, (\tau_h\tau_m/2mk_BT)^{1/2} \tag{3}$$

where $\tau_h = Q_h/\omega_h$ is the decay time of the oscillator with

5   motional mass m. Little is known about the intrinsic τ_h of Si

nano-oscillators at rf frequencies, since the only

measurements have been after metallization along the entire

length of the oscillator, which certainly decreases τ_h,

possibly drastically for structures of the size of interest.

10   At audio frequencies, $\tau_h > 1$ s is observed at room temperature

for pure Si cantilevers of thickness (60 nm) comparable to

those proposed here. In the examples, we conservatively use τ_h

$= 10^{-4}$ s. One of the first applications of FDOS will be to

measure this value. It is important to note that the force

15   sensitivity of rf oscillators is nearly the same as

audiofrequency cantilevers, since the lower τ_h of the former is

compensated by their lower mass. Thus the proposed designs,

with metal only over a small fraction of the length, have good

prospects of being the highest sensitivity design.

20   The Brownian motion of the mechanical oscillator can

contribute to the noise when measuring the coherently-driven

contribution to the oscillators displacement. Its minimization

is of interest. This motivates the application of any known

method of cooling to the oscillator and also the thermal

25   isolation of the oscillator from the sample, if it is to be

maintained at a different temperature. Such a barrier would

also allow a fluid to surround the sample, while allowing a

vacuum at the oscillator, ideally low enough that energy loss

to the residual gas is a negligible source of oscillator

5   damping. While in some applications a solid barrier may be

practical between the sample and the oscillator, the

improvement of the present method's sensitivity by close

approach of the sample and oscillators encourages the use of

geometries in which only vacuum (or a low viscosity fluid)

10   separates the sample and oscillator.   Minimizing the motional

mass of the oscillator (or moment of inertia for torsional

oscillators) and maximizing the mechanical ring-down time are

other design strategies for mitigating the effect of Brownian

noise on the signal-to-noise ratio. Crystalline silicon and

15   carbon nanotubes are examples of possible materials to form

the beam elements of the mechanical oscillators and methods of

fabrication are known for their suspension and for adding

(metallic) tip material to them.

Since heat will be deposited both in the sample and in

20   the oscillator by the driving fields, a practical design must

include thermal conduction to a heat sink to hold the

temperature increase of each to within acceptable limits. A

temperature rise is acceptable if it does not lead to sudden

destruction of the device or sample or to uselessly low

25   signal-to-noise ratio. The need to limit heating motivates the

use of materials for the oscillator beam and for the support

of oscillator and/or sample that have little absorption at the incident wavelengths. In this way the heating is confined to small thicknesses in contact with support material that can serve as a heat sink. High thermal conductivity is thus a

5 second desirable characteristic. . Crystalline materials such as diamond and calcium fluoride, for example, have the dual properties of high thermal conductivity and transparency to most wavelengths of spectroscopic interest.

A number of embodiments of the invention have been

10 described. Nevertheless, it will be understood that various modifications and enhancements may be made without departing from the following claims.